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**(54) Stabilization of sheet resistance of electrical conductors**

(57) A method for minimizing reaction between metal conductors and other metals to minimize change in sheet resistance of the conductors upon heat treatment which includes providing a substrate. The substrate is preferably one of a dielectric, a metal or a semiconductor. A metallic diffusion barrier layer, preferably one of TiN, TiW or TiWN and preferably having a thickness of from about 10 nanometers to about 100 nanometers, is deposited on the substrate, preferably by one of sputtering, electron beam evaporation or chemical vapor deposition. The exposed surface of the metallic diffusion barrier layer is treated with a plasma, preferably an oxygen plasma, a nitrous oxide plasma or a plasma of an oxygen-containing species. An electrical conductor, preferably one of aluminum, aluminum-metal alloys, copper or copper-metal alloys and preferably having a thickness of from about 100 nanometers to about 1200 nanometers, is then deposited on the plasma-treated surface of the metallic diffusion barrier layer. The layers can be formed as one of a blanket or continuous films over the substrate. The conductor can then be patterned.

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## Description

## BACKGROUND OF THE INVENTION

## 5 FIELD OF THE INVENTION

This invention relates to the stabilization of sheet resistance of for example Al-Cu alloy electrical conductors.

## BRIEF DESCRIPTION OF THE PRIOR ART

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Al-Cu alloy has been used as an electrical conductor in VLSI devices to take advantage of its low resistivity. However, Al-Cu alloy is quite active chemically and readily reacts with metals upon application of heat thereto, generally above 450°C. In order to circumvent this problem, TiN has been used as a diffusion barrier between Al-Cu alloy and other metals. However, post deposition heat treatment of the Al-Cu/TiN, such as spin-on-glass (SOG) cure, sintering, aluminum reflow and the like can increase the sheet resistance of, for example, Al-0.5%Cu (600 nm thickness)/TiN (50 nm thickness) by as much as fifteen percent. This poses a serious problem for devices where SOG (organic or inorganic) cure and aluminum reflow are used for dielectric planarization and via filling during fabrication.

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Most of the prior art relating to the improvement of TiN barrier properties is directed to preventing diffusion of aluminum into active silicon devices or into tungsten vias. In the prior art, the improvement of TiN barriers has mostly been achieved by optimizing the deposition parameters during TiN deposition, such as, for example, introducing oxygen flow during deposition or changing the substrate temperature or adding a substrate voltage bias. Some post-deposition treatments, such as, for example, thermal annealing and exposure to air have also been reported.

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The oxygen dosing during TiN deposition is not desirable because oxygen may contaminate the titanium sputtering target, form titanium oxide particles and increase the sheet resistance of TiN. Changing deposition temperature may induce change in other properties of TiN, such as stress and grain size, making it difficult to optimize these parameters at the same time. Adding substrate bias induces ion bombardment of the TiN layer, this possibly resulting in radiation damage to the existing devices. Post-deposition treatment involves additional processing steps and hence increases the process cycle time. Moreover, thermal annealing (densification) of TiN can only be accomplished at the contact level where Al-Cu alloy is not present. It has been determined by applicants that exposure of TiN to air for 24 hours does not improve the barrier properties.

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## SUMMARY OF THE INVENTION

In accordance with the present invention, the resistance of an electrical conductor, such as aluminum, copper and alloys thereof, such as, for example, Al-Cu alloy, is stabilized by the use of a plasma beam, preferably oxygen, after a metallic diffusion barrier layer deposition thereon, preferably TiN, whereby the barrier properties of the TiN are improved. As a result, the sheet resistance of Al-Cu/TiN remains the same after thermal cycling. Advantages derived by this procedure are that, since the plasma treatment is not effected during TiN deposition, there is no contamination/particle problem as discussed above. Further, since the plasma is a low energy ion beam, sufficient to provide from about 30 to about 50 percent oxygen in the surface region of the metallic diffusion barrier layer, it only interacts with the surface region of the TiN to a depth of up to about 50Å. Consequently, the bulk of the TiN still remains metallic and the sheet resistance of the TiN is not changed significantly. On the other hand, in the case of an oxygen plasma, for example, the surface region is believed to be a Ti-N-O layer at the surface of the TiN which is formed by the oxygen plasma/TiN interaction and is thick enough to block the reaction between Al-Cu alloy and TiN while at the same time thin enough to allow current tunneling. Still further, the plasma treatment can be conveniently performed in a resist ash chamber, which is available in the fabrication environment. The total ash time (plasma treatment time) can be very short (less than one minute), so the throughput is not severely compromised. If process integration is required, a separate oxygen plasma chamber can be readily added to the existing TiN sputtering system.

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Briefly, the procedure in accordance with the present invention requires providing a substrate, preferably one of a dielectric, a metal or a semiconductor. A metallic diffusion barrier layer, preferably one of TiN, TiW or TiWN and preferably having a thickness of from about 10 nanometers to about 100 nanometers, is deposited on the substrate, preferably by one of sputtering, electron beam evaporation or chemical vapor deposition. The exposed surface of the metallic diffusion barrier layer is treated with a plasma, preferably an oxygen plasma, a nitrous oxide plasma or a plasma of an oxygen-containing species. An electrical conductor, preferably one of aluminum, aluminum-metal alloys, copper or copper-metal alloys and preferably having a thickness of from about 100 nanometers to about 1200 nanometers, is then deposited on the plasma-treated surface of the metallic diffusion barrier layer. The layers can be formed as one of a blanket or continuous films over the substrate. The electrical conductor and the diffusion barrier can then be patterned.

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## DESCRIPTION OF THE PREFERRED EMBODIMENT

A 50 nanometer thick layer of TiN was first deposited on several substrates of silicon dioxide. Then some of the substrates with the layer of TiN thereon were subjected to an oxygen plasma treatment in a resist ash chamber using a single, double and triple Gasonic process, using the Branson recipe for 30 and 60 minute time periods and with no ashing. The Branson recipe is as follows:

Oxygen	650 SCCM (standard cubic centimeters)
RF Power	1000 watts
Pressure	1.15 Torr
Time	(see chart below)

The Gasonic Process is as follows:

Oxygen	5 SCCM
Nitrous Oxide	0.5 SCCM
Pressure	1.75 Torr
RF Power	1000 watts
Time	50 seconds

Then wafers with ash by each of the above procedured for the times listed in the chart below and without ash were covered with with a 600 nanometer thick layer of Al-0.5%Cu alloy by sputtering. The sheet resistance of the wafers was measured. After SOG cure heat treatment at 450°C for one hour, the sheet resistance of the wafers was again measured and a comparison was made with the measured sheet resistance before the SOG cure. The resistance increase (RI) in percentage was tabultaed as follows:

Ash Recipe	RI(TiN)	RI(Al-Cu/TiN)	Time
Single Gasonic	10.6	0.35	50 seconds
Double Gasonic	16.3	0	100 seconds
Triple Gasonic	35.4	1.3	150 seconds
30 min. Branson	8.4	1.3	30 minutes
60 min. Branson	11.4	1.1	60 minutes
No ashing	1.5	10.5	

It can be seen that plasma treatment or ashing resulted in a negligible increase in resistance as compared with no ashing.

Though the invention has been described with reference to a specific preferred embodiment thereof, many variations and modifications will immediately become apparent to those skilled in the art. It is therefore the intention that the appended claims be interpreted as broadly as possible in view of the prior art to include all such variations and modification.

## Claims

1. A method for minimizing reaction between metal conductors and other metals to minimize change in sheet resistance of said conductors upon heat treatment, comprising the steps of:

providing a substrate;  
depositing a metallic diffusion barrier layer on said substrate;  
treating the exposed surface of said metallic diffusion barrier layer with a plasma; and  
depositing an electrical conductor on the plasma-treated surface of said metallic diffusion barrier layer.

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2. The method of claim 1 wherein said substrate is one of a dielectric, a metal or a semiconductor.

3. The method of claim 1 wherein said metallic diffusion barrier layer is one of TiN, TiW or TiWN.

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4. The method of claim 2 wherein said metallic diffusion barrier layer is one of TiN, TiW or TiWN.

5. The method of claim 1 wherein said plasma is essentially one of an oxygen plasma, a nitrous oxide plasma or a plasma of an oxygen-containing species.

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6. The method of claim 2 wherein said plasma is essentially one of an oxygen plasma, a nitrous oxide plasma or a plasma of an oxygen-containing species.

7. The method of claim 3 wherein said plasma is essentially one of an oxygen plasma, a nitrous oxide plasma or a plasma of an oxygen-containing species.

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8. The method of claim 4 wherein said plasma is essentially one of an oxygen plasma, a nitrous oxide plasma or a plasma of an oxygen-containing species.

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9. The method of claim 1 wherein said conductor is taken from the class consisting of aluminum, aluminum-metal alloys, copper and copper-metal alloys.

10. The method of claim 2 wherein said conductor is taken from the class consisting of aluminum, aluminum-metal alloys, copper and copper-metal alloys.

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11. The method of claim 4 wherein said conductor is taken from the class consisting of aluminum, aluminum-metal alloys, copper and copper-metal alloys.

12. The method of claim 8 wherein said conductor is taken from the class consisting of aluminum, aluminum-metal alloys, copper and copper-metal alloys.

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13. The method of claim 12 wherein said metallic diffusion barrier layer is deposited by one of sputtering, electron beam evaporation or chemical vapor deposition.

14. The method of claim 1 wherein the thickness of said metallic diffusion barrier is from about 10 nanometers to about 100 nanometers.

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15. The method of claim 14 wherein the thickness of said metallic diffusion barrier is from about 10 nanometers to about 100 nanometers.

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16. The method of claim 1 wherein the thickness of said conductor is from about 100 nanometers to about 1200 nanometers.

17. The method of claim 15 wherein the thickness of said conductor is from about 100 nanometers to about 1200 nanometers.

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18. The method of claim 1 wherein said layers are formed as one of a blanket or continuous films over said substrate.

19. The method of claim 17 wherein said layers are formed as one of a blanket or continuous films over said substrate.

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20. The method of claim 1 further including the step of patterning said conductor.

21. The method of claim 19 further including the step of patterning said conductor.

22. The method of claim 1 wherein said plasma is an oxygen plasma providing from about 30 to about 50 percent oxygen in a surface region of said metallic diffusion barrier layer having a thickness sufficient to substantially block reaction between said electrical conductor and said metallic diffusion barrier layer up to about 50A.

5 23. The method of claim 17 wherein said plasma is an oxygen plasma providing from about 30 to about 50 percent oxygen in a surface region of said metallic diffusion barrier layer having a thickness sufficient to substantially block reaction between said electrical conductor and said metallic diffusion barrier layer up to about 50A.

24. A conductor produced by the method of any preceding claim.

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25. A semi-conductor device including a conductor as claimed in claim 24.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 96 10 4337

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 295 (E-1094), 26 July 1991 & JP 03 104220 A (FUJITSU LTD), 1 May 1991, * abstract *	1-13,24, 25	H01L21/285
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 383 (E-1116), 27 September 1991 & JP 03 153077 A (SEIKO EPSON CORP), 1 July 1991, * abstract *	1-8,24, 25	
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A	US 5 187 557 A (ZENKE MASANOBU) * the whole document *	1,14-19	
A	CA 1 275 332 A (HO VU Q ;NORTHERN TELECOM LTD (CA)) * page 2, paragraph 2 - page 4, paragraph 1 *		
A	S. IWABUCHI, S. SHIMA, T. MAEDA, T. MORIYA: "A Highly Reliable Pure Al Metallization with Low Contact Resistance Utilizing Oxygen-Stuffed TiN Barrier Layer" 1986 SYMPOSIUM ON VLSI TECHNOLOGY DIGEST OF TECHNICAL PAPERS, vol. V-4, 28 - 30 May 1986, pages 55-56, XP002054322 * the whole publication *		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01L
Place of search THE HAGUE		Date of completion of the search 19 February 1998	Examiner Königstein, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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